PATENT SPECIFICATION

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COMPLETE SPECIFICATION

NO DRAWINGS

Process for the Preparation of Emulsifiers for Ointment Base Compositions

We, DEHYDAG DEUTSCHE HYDRIERWERK GmbH., a German Company, of 67, Henkelstrasse, Dusseldorf, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for the production of emulsifiers for ointment bases.

The present invention provides a composition for an ointment base which contains a mixed ester from a pentaerythritol-di-fatty acid ester and a citric acid-di-fatty alcohol ester in the molar ratio 1:1. These compositions are distinguished by being odourless and having a high, steady water-binding capacity.

It has been found that specially valuable products with the above-described valuable properties are obtained when mixed ester products which possess lipophilic residues simultaneously with both the polybasic citric acid residue and the polyhydric alcohol residue are prepared by an esterification process under an inert gas. Those products are particularly advantageous which are derived from pentaerythritol as the polyhydric alcohol.

The particular technical value of the compositions prepared according to the process of the invention rests not only on their structure and the advantages resulting therefrom, but also on the ease of production. It is known that the preparation of citric acid esters by the usual esterification methods causes difficulties, since the citric acid on relatively long heating is converted partly into unsaturated aconitic acid with splitting off of water which leads to troublesome resinous compounds in the further course of the reaction.

The surprising discovery has now been made that these difficulties may be avoided if aqueous citric acid is used for the esterification. The use of an aqueous component in the esterification proless is entirely contrary to the usual customs, since it normally causes a delay in the course of the reaction and therefore favours side reactions. The esterification is carried out by adding to the given fatty alcohol, heated at 140-170°C., for the most part at 160°C., and under a pressure of about 25 mm Hg, only as much aqueous citric acid as reacts simultaneously with the alcohol. Every side reaction and consequently resinification is prevented by the rapid esterification and a satisfactory light-coloured esterification product is obtained.

The preparation of the second esterification product, the pentaerythritol di-fatty acid ester, takes place by the usual process, in which case preference is given to the production by inter-esterification of a fatty acid methyl ester, since in this way especially light-coloured products with an acid value below 1 are obtained.

Examples of the preparation of the pentaerythritol di-fatty acid ester include:—

(i) 136 kg pentaerythritol with 470 kg. coconut fatty acid methyl ester and 1.8 kg. sodium methylate as esterification catalyst are placed in an agitator.

The contents of the apparatus are highly heated with stirring. At approximately 70°C. methyl alcohol is distilled from the reaction mixture. When no further methyl alcohol is distilled over the final residues of alcohol is removed in vacuo. After 2 hours the acid number has dropped below 2 and the esterification is concluded.

(ii) 100 kg coconut fatty acid are employed. With stirring there are added; 31 kg pentaerythritol, 200 kg 50% soda lye as esterification catalyst. Esterification is

[Price 4s. 6d.]

Price 25p

effected for one hour at 180°C. and for a further 5 hours at 180°-190°C. at a pressure of approximately 50 mms. During this time a weak flow of nitrogen is passed through the liquid by means of a dip tube serving as a boiling capillary. The esterification is concluded when the acid number of the reaction mixture has dropped below 2.

The interesterification of the above two esterification products is carried out in an inert atmosphere and is concluded when the acid value of the reaction mixture falls below one. This interesterification process may be carried out at reduced pressure and elevated temperature and preferred values for the pressure and temperature are 25 mms. at Hg and 180° to 190°C., respectively. Catalysts are not generally required.

Accordingly the present invention provides a process for the preparation of emulsifiers for ointment bases in which a mixed ester is prepared by an interesterification process under an inert gas from a citric acid-di-fatty alcohol ester prepared by esterification of a fatty alcohol with aqueous citric acid and a pentaerythritol-di-fatty acid ester in the molar ratio of 1:1.

The citric acid mixed esters obtainable using the process of the invention from a pentaerythritol-di-fatty acid ester and a citric acid-di-fatty alcohol ester display very valuable properties. The stability to temperature of the emulsions produced therewith is outstanding, the limit of temperature being especially high, at about 50°C. The water-binding capacity is likewise considerably better and not only are relatively large amounts of water absorbed substantially more rapidly, but the larger total amount of water may also be incorporated in larger portions. In addition, the ointments obtained using the usual qualities of Vaseline (Registered Trade Mark) are pure white and no longer yellow as hitherto, and are furthermore practically odourless and easily and durably perfumed. A further important advantage is that they are easier to preserve and have far better keeping quality on fairly long storage. The ointments obtained also display a smoother softer structure, a more pliable consistency, i.e. they do not stick, provide a subjectively more pleasant impression on the skin and are absorbed more easily by the skin. The ointments prepared with the products according to the invention are dermatologically completely satisfactory.

Example 1. (a) *Preparation of a citric acid dioctadecyl ester.*

115 parts by weight of octadecyl alcohol of hydroxyl number 206 and 54 parts by weight of aqueous citric acid (consisting of 44 kg of citric acid dissolved in 10 kg of water) are reacted so that only as much aqueous citric acid is added as can react with the given alcohol at one time. The course of the esterification can be followed by the water of reaction which passes ver. The ester is light in colour, has an esterification value of 241 and an acid value of 80 to 85, as is necessary for the further preparation of the mixed condensate.

(b) *Preparation of a pentaerythritol di-coconut oil fatty acid ester.*

76 parts by weight of pentaerythritol are reacted with 260 parts by weight of coconut oil fatty acid methyl ester with a saponification value of 240 and 1 part by weight of sodium methylate as esterification catalyst until the acid value has fallen below 2. The pentaerythritol di-coconut oil fatty acid ester formed is freed from the accompanying soap with 1% of fuller's earth.

(c) *Preparation of the citric acid mixed condensate.*

140 parts by weight of citric acid dioctadecyl ester from (a) and 115 parts by weight of pentaerythritol di-coconut oil fatty acid ester from (b) are esterified in an atmosphere of inert gas at a pressure of 25 mms of Hg and a temperature in the range 180°-190°C. until the acid value of the reaction product lies below 1. After the esterification is finished, the mixed ester is bleached with 0.1% (referred to the total weight) of 40% hydrogen peroxide. A mixed ester of wax-yellow colour with an acid value below 1, a saponification value of 224 and a hydroxyl value of 75 is obtained.

(d) *Preparation of an ointment base.*

35 parts by weight of vaseline
30 " " " " decyloleate
6 " " " " cetyl alcohol
5 " " " " ozocerite, white, 70/72°
5 " " " " hard paraffin, 50/52°
5 " " " " paraffin, viscous
2 " " " " aluminium stearate

with addition of 12 parts by weight of the citric acid mixed ester according to (c) above are melted together on the water bath, stirred until homogeneous and allowed to cool. An ointment base is obtained which posesses a high water absorption capacity.

After suitably perfuming or after addition of pharmaceutically active substances, the ointment base may be used as such. But there may also be incorporated in the ointment base up to three times its amount of water, when salves (water in oil emulsions) of various consistency are obtained. The amount of water used depends upon the special purpose for which the salve is to be used and may be adjusted to any desired use.

Example 2.

Mixed esters from the following pairs of esters may be prepared similarly: citric acid dilauryl ester and pentaerythritol-distearic acid ester, citric acid-dilauryl ester and pentaerythritol-dicoconut oil fatty acid ester,

citric acid-di-Guerbet alcohol (C_{32}) ester and pentaerythritol-distearic acid ester, citric acid-dioctadecanediol ester and pentaerythritol-di-coconut oil fatty acid ester, citric acid-dioctadecanediol ester and pentaerythritol-distearic acid ester, citric acid-didodecyl ester and pentaerythritol-dicoconut oil fatty acid ester.

Among all the citric acid mixed esters specified, the mixed ester from citric acid-dioctadecyl (stearyl) ester and pentaerythritol-di-coconut oil fatty acid ester is most suitable for use as an emulsifier in ointment bases.

WHAT WE CLAIM IS:—

1. A process for the preparation of emulsifiers for ointment bases in which a mixed ester is prepared by an esterification process under an inert gas from a citric acid-di-fatty alcohol ester, prepared by esterification of a fatty alcohol with aqueous citric acid, and a pentaerythritol-di-fatty acid ester in the molar ratio of 1:1.

2. A process as claimed in claim 1 in which the citric acid-di-fatty alcohol ester is citric acid-dioctadecyl (stearyl) ester.

3. A process as claimed in any preceding claim in which the pentaerythritol-di-fatty acid ester is pentaerythritol di-coconut oil fatty acid ester.

4. A process for the preparation of ointment bases substantially as hereinbefore described with reference to the Examples.

5. Emulsifiers for ointment bases when prepared by the process of any one of claims 1 to 3.

6. Ointments containing the emulsifiers claimed in claim 5.

W. P. THOMPSON & Co.,
12, Church Street, Liverpool, 1.
Chartered Patent Agents.

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